

PATENT SPECIFICATION

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 (72) Inventor IAN ROBERT WHEELER



(54) PRODUCTION OF LOW MOLECULAR WEIGHT URETHANE POLYMER DISPERSIONS

(71) We, CIBA-GEIGY AG, a Swiss Body Corporate, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 The present invention relates to dispersions of solids in liquids and, in particular, to pigment dispersions in non-aqueous solvents.

In our British Patent Specification No. 1,445,104, there are described and claimed flocculation-resistant dispersions of a solid in a liquid, said dispersions comprising a particulate solid material, an organic liquid an, as stabiliser, a material which a) contains groups which are solvated by organic liquid, b) contains two or more urethane groups and c) contains no significant proportion of basic amino groups.

10 The preferred urethane stabilisers of Specification No. 1,445,104 are those derived from toluene-diisocyanates, short-chain diols and long-chain alcohols in the respective mole ratios in the range of 2:1:2 to 4:3:2 and these preferred urethanes are particularly useful in producing stabilised pigment dispersions for 15 ultimate incorporation in oil based decorative paints and publication gravure ink systems.

15 We have been using the preferred urethane stabilisers of Specification No. 1,445,104 to produce pigment dispersions for incorporation into hydrocarbon-based application systems. Since the principal solvent in such systems is an aliphatic or aromatic hydrocarbon, or a mixture thereof, there is a clear incentive to produce a urethane stabiliser, of the above preferred type, directly in such a solvent, rather than utilising the procedures described in Specification No. 20 1,445,104 in which the stabiliser is prepared in a polar, oxygenated solvent, followed by removal of that solvent by distillation and incorporation of the stabiliser in the hydrocarbon solvent.

25 This objective proved very difficult to attain, apparently because of the poor solubility of some of the reagents, particularly the low molecular weight diols, in aliphatic hydrocarbons. At best, applying very precise control over the reaction conditions and introducing the reagents or reaction intermediates at various stages of reaction, there were obtained only hazy solutions, containing particles of urethane visible to the naked eye. Such products exhibited poor properties in application, moreover the presence of particles in stabiliser solutions rendered them difficult to pump due to blockages in the pipelines. At worst, there occurred 30 irreversible precipitations from, or gelation of, the reaction mixture.

35 We have now found a process for the production of the above preferred urethane stabilisers by the use of which the aforesaid problems are overcome and which provides stabiliser solutions eminently suitable for the production of 40 pigment dispersions directly compatible with hydrocarbon solvent-based applications media.

45 Accordingly, the present invention provides a process for the production of a urethane polymer comprising polymerising, until no free isocyanate can be detected, a reaction mixture containing a diisocyanate, an aliphatic diol having 2 to 4 carbon atoms and a mono hydroxy compound having from 10 to 22 carbon atoms, in the respective mole ratios of 2:1:2 to 4:3:2, in a hydrocarbon solvent containing from 7.5—50%, preferably 20—25% by weight, based on the total weight of solids, of a primer (as hereinafter defined).

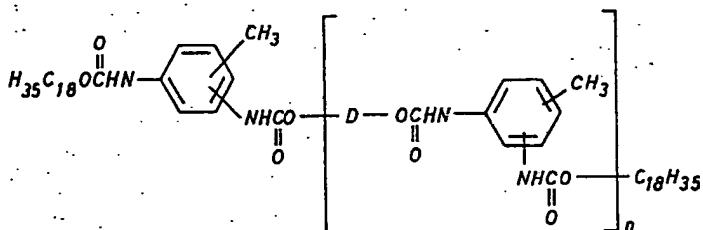
The primer is a pre-formed urethane condensation product either produced

by the process of this invention or by a process described and claimed in British Patent Specification No. 1,445,104. Preferably it is a condensation product of tolylene diisocyanate, oleyl alcohol and a low molecular weight diol such as ethylene glycol.

5 For preparation of the urethane polymers of the present invention, examples of suitable diisocyanates include tolylene diisocyanates, especially commercially available mixtures of tolylene-2,4- and -2,6-diisocyanates, hexamethylene diisocyanates and diphenylmethane diisocyanate; suitable 10-22C alcohols are decanol, dodecanol, cetyl alcohol, stearyl alcohol, oleyl alcohol and behenyl alcohol. Diols having 2-4C include ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,2-diol, butane-1,3-diol, butane-1,4-diol and butane-2,3-diol.

10 Examples of suitable hydrocarbon solvents are the substantially aliphatic hydrocarbons commercially available as fractions of selected boiling point ranges from 40°C to 260°C, such as that known as white spirit and the SBP solvents of Shell Mex Ltd. and British Petroleum Ltd. Suitable aromatic hydrocarbons are benzene, toluene, the isomeric xylenes and other alkyl benzene derivatives.

15 The process of the present invention is of particular interest for the production of urethane polymers of the formula:-



20 wherein D is the residue of a dihydroxy compound having a low solubility of the aliphatic hydrocarbon solvent and is preferably derived from an aliphatic diol having 2-4C atoms.

n is from 1 to 3 especially 2.

25 Such preferred urethane polymers are based on diols having a short chain length and hence of low solubility in hydrocarbons and which, while having excellent performance as dispersion stabilisers, are very difficult to produce directly in hydrocarbon solvents.

30 The priming urethane may be derived from the same or different precursors used to produce the urethane polymer, provided that the priming urethane is one which has sufficient solubility in hydrocarbons to avoid an appreciable precipitation of polymer during the process of the invention. With this proviso in mind the priming urethane may be selected from those described and claimed in British Patent Specification No. 1,445,104: and prepared from the appropriate isocyanate and hydroxy compound precursors. Examples of suitable isocyanate precursors are hexamethylene diisocyanate, diphenylmethane diisocyanate, tris(4-isocyanatophenyl)methane but tolyene-2,4-diisocyanate, optionally containing a proportion of the 2,6-isomer, is preferred.

35 Examples of hydroxy compound starting materials for production of primers are n-octanol, n-decanol, n-dodecanol, n-octadecanol, myristyl, cetyl, stearyl, oleyl, and behenyl alcohols. Of these oleyl alcohol is preferred.

40 Examples of diols for production of primers include ethylene glycol, propane 1,2-diol, propane 1,3-diol, and the isomeric butane, pentane and hexane diols; diethylene glycol and thioglycol, but ethylene glycol is preferred.

45 Preferred priming urethanes are those derived from the above mentioned constituents for the products of the process of this invention, with the same mole ratio range. These may have been prepared in a polar solvent, for example an aliphatic ketone, such as acetone or ethyl methyl ketone, and then transferred into an aliphatic hydrocarbon solvent. Alternatively, they may be prepared by the process of the present invention.

50 An additional feature of the invention is that the primer is advantageously chemically identical with the stabiliser being manufactured. Not only does this guarantee optimum stabilising capability, it also provides a substantial economy as only one initial batch of primer requires to be prepared in a polar solvent and transferred into an aliphatic hydrocarbon solvent. Subsequently batches are conveniently primed by using a portion of the previous batch.

Desirably, in order to achieve optimum reaction rate and freedom from precipitation problems, the process of the present invention is effected at a temperature within the range of from 80° to 120°C, more preferably within the range of from 90° to 105°C.

Too low a reaction temperature is to be avoided since the reaction time is considerably extended and the likelihood of precipitation of the reagents or partially formed product from the solvent is increased.

Too high a reaction temperature however, is also to be avoided as it has been found to lead to deterioration of the properties of applications systems in which such urethanes are incorporated.

The presence of too much solvent in the process of the present invention is to be avoided because it surprisingly leads to precipitation problems. Satisfactory results are achieved by using an initial solvent level of 20% weight/weight on total weight of reaction mixture, with subsequent dilution to 40%—50% weight/weight, at the end of the process.

The urethane polymers produced according to the process of the present invention are particularly useful for the production of pigment dispersions in a medium which is suitable for direct incorporation into surface coatings.

Accordingly, the present invention also provides a pigment dispersion, comprising a pigment and, as stabiliser, a solution of a urethane polymer as produced according to the process of the present invention.

Pigments of particular interest include organic pigments, for instance azo and azomethine pigments, metal or metal free phthalocyanines, optionally halogen-substituted polycyclic pigments such as quinacridones, dioxazines, vat dye-stuffs, anthraquinones and isoindolinones, and salts of basic pigments precipitated with the heteropoly acids of phosphorous, tungsten and molybdenum.

Inorganic pigments may also be used such as titanium dioxide and red and yellow iron oxides. Carbon black may also be used.

Pigment dispersions according to the invention may be prepared by blending the pigment and the stabilizer solution by any convenient method, although the following techniques are of special interest:—

(a) Ball-milling a mixture of pigment, organic solvent and urethane polymer solution for an extended period.

(b) Flushing the pigment from aqueous press-cake into solvent and then adding the urethane polymer solution at this stage.

(c) In-situ preparation of the urethane polymer from its starting-materials during the treatment of pigment as in either of steps (a) or (b).

The relative proportions of the components of the dispersions according to the invention are advantageously chosen so that the amount of the urethane polymer is within the range from 5% to 200% by weight based on the pigments in the dispersion.

Desirably the dispersions contain from 10% to 60% by weight of pigments based on the total weight of the dispersion.

Advantages of the process of the present invention over previously known processes are e.g.

a) the urethane polymer stabiliser is produced in a hydrocarbon solvent which forms part of many final surface coating media thereby avoiding distillation stages which had been previously necessary,

b) the process of the invention is reliable, easily-controlled, optionally continuous and yields a high solids, pumpable, pourable stabiliser solution, and

c) Only one priming urethane need be produced since a urethane polymer solution prepared according to the invention can thereafter admirably fulfil the 'priming' function.

The pigment dispersions of the present invention are particularly suitable for direct incorporation into surface coatings based on hydrocarbon solvents such as long oil alkyd in white spirit decorative paints and zinc-calcium resinate (with or without phenolic modified resinate) in aliphatic, aromatic or mixed hydrocarbon solvent publication rotogravure inks.

The following Examples further illustrate the present invention. Parts and percentages shown therein are by weight.

Example 1.

Preparation of 3:2:2 mole ratio

TDI:EG:OA urethane primer in EMK followed by transfer into white spirit solution and subsequent use as primer for the preparation of the same urethane in white spirit.

A) the following dried reagents were charged to a vessel fitted with agitator and reflux condenser:

	oleyl alcohol (OA)	281.4 parts	
	ethylene glycol (EG)	62 parts	
5	ethyl methyl ketone	300 parts	5

The temperature was raised to 80°C and 261 parts of a commercial 80:20 mixture of 2,4- and 2,6-tolylene diisocyanate (TDI) added over 1 hour. This temperature was maintained for approximately 8 hours until no free isocyanate could be detected by infra-red spectroscopy. The product was a clear solution, free of solid matter. The ethyl methyl ketone was removed by rotary evaporation and sufficient white spirit added to form a clear, pale amber solution of 50% solids content.

10 B) 211.2 parts of the urethane solution produced in Part A of this Example were added to a vessel containing 145.6 parts oleyl alcohol, and 32.9 parts ethylene glycol. The temperature was raised to 95°C and maintained during 15 the addition of 138.3 parts of tolylene diisocyanate over 1 hour, and subsequently for approximately 8 hours, until no free isocyanate could be detected by infra-red spectroscopy. 316.8 parts white spirit were added to form a clear, pale amber solution of 50% solids content.

20 C) 30 parts of the urethane solution produced in part B of this example were ball milled for 16 hours with 30 parts of the beta copper phthalocyanine blue pigment produced in Example 1 of British Patent Application No. 37106/75 (Serial No. 1,501,184) and 40 parts of white spirit, to form a well deflocculated dispersion. The flow of this dispersion was 10.5 seconds measured using a No. 3 Zahn Cup, and the degree of dispersion was 8:7.5:7 by Hegmann Gauge. The strength obtained from 1:25 reduction of the dispersion in white alkyd paint was excellent 25 being similar to that obtained from the product of Example 2 of British Patent Application No. 37106/75 (serial No. 1,501,184).

Example 2.

Use of a Primed Batch as a Primer.

30 The method of Example 1B was repeated with the substitution of 211.1 parts of the product of Example 1A by an equal weight of the product of Example 1B. A pigment dispersion prepared from the product of this example by the method of Example 1C was a well deflocculated dispersion having a flow value of 8 seconds (No. 3 Zahn cup), and a degree of dispersion of 8:7.7 (Hegmann Gauge). Its 35 strength in 1:25 reduction was, 0—5% stronger than the product of Example 1(C).

Examples 3—5.

Variation of Primer Level.

40 The method of Example 1B was repeated with the substitution of 211.2 parts of the product of Example 1A by 51.4 parts, 111.8 parts and 316.8 parts respectively (corresponding to 7.5%, 15% and 50% by weight respectively) of dry preformed urethane calculated on the total batch weight less solvent.

45 From the properties of these urethane solutions and the dispersions produced from them by the method of Example 1C, it can be seen in Table 1 that use of too low a level of preformed urethane does not lead to the preparation of clear urethane solutions free of solid matter, while too high a level is wasteful of reactor volume. The optimum level of preformed urethane may be found by experiment for other urethane types in other hydrocarbon solvents.

Example 6.

Variations of Molar Proportions of Reagents.

50 *Preparation of 2:1:2 mole ratio TDI:EG:OA urethane in EMK, transfer into white spirit, and use to prepare more urethane of the same type in white spirit.*

A) 261 parts tolylene diisocyanate, 422.1 parts oleyl alcohol, 46.5 parts ethylene glycol and 182.4 parts ethyl methyl ketone were reacted and transferred into white spirit to give a solution of 50% solids according to the method of Example 1A.

55 B) 486.4 parts of the urethane solution produced in Part A of this example were added to a vessel containing 422.1 parts oleyl alcohol, and 46.5 parts ethylene glycol. 261 parts of toluene diisocyanate were added and reacted according to the method of Example 1B. 729.6 parts of white spirit were added to form a product of 50% solids content, whose properties are described in Table 2.

*Comparative Example 6.1.**Attempted direct preparation of 2:1:2 urethane.*

Example 6B was repeated with 182.4 parts white spirit in place of the product of Example 6A. A translucent yellow product with properties described in Table 2 was obtained. The properties of the pigment dispersion produced by the method of Example 1C are given in Table 2.

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Example 7.

Preparation of 4:3:2 molar ratio TDI:EG:OA urethane by priming with 3:2:2: urethane. 481.6 parts of the product of Example 1B were added to a vessel containing 93 parts of ethylene glycol and 281.4 parts of oleyl alcohol. The temperature was raised to 95°C, and maintained during the addition of 348 parts of tolylene diisocyanate over 1 hour, and subsequently for approximately eight hours until no free isocyanate could be detected in infra-red spectroscopy. During this time further white spirit was added as required, to maintain efficient stirring, and to achieve a final solids content of 50%.

10

The properties of this urethane solution, and the dispersion produced from it by the method of Example 1C are contained in Table 2.

15

*Comparative Example 7.1.**Attempted direct preparation of 4:3:2 urethane.*

Example 7 was repeated with 180.6 parts white spirit in place of the product of Example 1B. A clear urethane solution free of solid matter could not be obtained.

20

*Example 8.**Use of a urethane which can be prepared directly in white spirit to prepare one which cannot.*

A) Using the method of Example 1A, 261 parts tolylene diisocyanate, 281.4 parts oleyl alcohol, 104 parts neopentyl glycol and 161.6 parts white spirit were used to prepare a 50% solids content, clear urethane solution free of solid matter.

25

B) 211.2 parts of the product of Part A of this example were reacted with 145.6 parts oleyl alcohol, 32.9 parts ethylene glycol, and 138.3 parts tolylene diisocyanate by the method of Example 1B. A slightly cloudy but pumpable 50% solids content urethane solution, free of precipitated material was obtained. The properties of this urethane solution and the dispersion produced from it by the method of Example 1C are contained in Table 2.

30

*Example 9.**Use of 3:2:2 TDI:EG:OA urethane prepared in EMK and transferred into SBP3, as a primer for the preparation of the same urethane in SBP3.*

35

A) The method of Example 1A was followed until the solvent removal stage, when SBP3 (a largely aliphatic hydrocarbon solvent blend of boiling point range 102–122°C) was used in place of white spirit to produce a clear pale yellow solution of 50% solids content.

40

B) 211.2 parts of the urethane solution produced in Part A of this Example were substituted for the product of Example 1A in the method of Example 1B, with SBP3 solvent in place of white spirit, to produce a slightly cloudy, but pumpable 50% solids content urethane solution, free of precipitated solid material.

45

This urethane solution was used in the method of Example 1C, with SBP3 as solvent in place of white spirit, to produce a well deflocculated pigment dispersion with a No. 3 Zahn Cup viscosity of 9 seconds, and of excellent strength when incorporated in publication rotogravure ink media.

45

Example 9B was repeated with 79 parts SBP3 in place of the product of Example 9A. An unpumpable plastic mass in solvent was obtained.

50

TABLE I

Example No.	Process Variation	Appearance	PIGMENT DISPERSION *		
			Flow Zahn Cup No. 3 (secs.)	Degree of Dispersion (Hegmann Gauge)	Strength 1:25 Reduction in white alkyd paint
1B	—	Clear, pale amber solution	10.5	8:7.7	Control
2	Primed batch as primer	Clear, pale amber solution	8	8:7.7	0-5% strong
3	7.5% primer level	Clear, amber fluid; some precipitated solid.	12	8:7.7	5-10% weak
4	15% primer level	Clear amber fluid; a little solid	11	8:7.7	0-5% weak
5	50% primer	Clear, deep amber solution	11	8:7.7	0-5% weak

* Prepared according to the method of Example 1C.

TABLE II

Example No.	Type	PIGMENT DISPERSION *		
		Flow Zahn Cup No. 3 (secs.)	Degree of Dispersion (Hegmann Gauge)	Strength relative to that of Ex. 1C. 1:25 reduction in white alkyd paint
URETHANE				
6	Primed 2:1:2 mole ratio TDI:EG:OA	Translucent yellow solution; no solid.	15 (slightly thixotropic)	8:7:7
6.1	Unprimed 2:1:2 mole ratio TDI:EG:OA	Translucent yellow solution; slight precipitate.	Too thixotropic—no reading	8:7:7
7	4:3:2 mole ratio primed with 3:2:2 urethane	Almost clear solution; a little solid.	40 (moderately thixotropic)	8:7:7
7.1	Unprimed 4:3:2 mole ratio	Product precipitated during reaction	—	—
8	3:2:2 mole ratio primed with unprimed 3:2:2 TDI:NPG:OA	Translucent fluid, free of solid	10	8:7:7
				Equal

* Prepared according to the method of Example 1C.

WHAT WE CLAIM IS:—

5 1. A process for the production of a urethane polymer, comprising polymerising, until no free isocyanate can be detected, a reaction mixture containing a diisocyanate, an aliphatic diol having 2 to 4 carbon atoms and a mono hydroxy compound having from 10 to 22 carbon atoms, in the respective mole ratios of 2:1:2 to 4:3:2, in a hydrocarbon solvent containing from 7.5 to 50%, by weight, based on the total weight of solids, of a primer (as hereinbefore defined).

10 2. A process as claimed in claim 1 wherein the hydrocarbon solvent contains from 20 to 25% by weight, based on the total weight of solids, of a primer.

15 3. A process as claimed in claim 1 or 2 wherein the primer is a pre-formed urethane condensation product either produced by the process of this invention or by a process described and claimed in British Patent Specification No. 1,445,104.

20 4. A process as claimed in any of the preceding claims wherein the diisocyanate reactant is a tolylene diisocyanate, hexamethylene diisocyanate, or diphenylmethane diisocyanate.

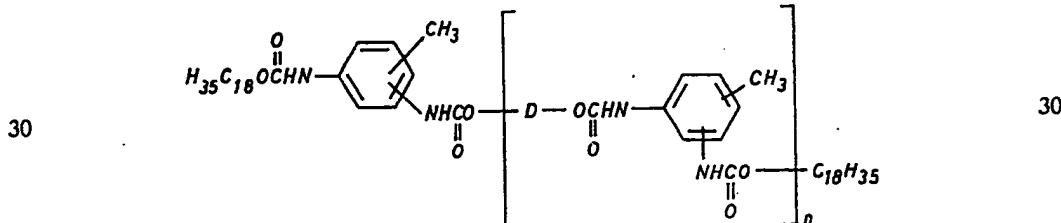
25 5. A process as claimed in claim 4 wherein the tolylene diisocyanate is a commercially available mixture of tolylene-2,4- and 2,6-diisocyanates.

6. A process as claimed in any of the preceding claims wherein the 10—22C alcohol reactant is decanol, dodecanol, cetyl alcohol, stearyl alcohol, oleyl alcohol or behenyl alcohol.

25 7. A process as claimed in any of the preceding claims wherein the 2—4C diol is ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,2-diol, butane-1,3-diol, butane-1,4-diol or butane-2,3-diol.

8. A process as claimed in any of the preceding claims wherein the hydrocarbon solvent is a commercially available aliphatic fraction having a boiling range of from 40°C to 260°C., benzene or toluene.

25 9. A process as claimed in any of the preceding claims wherein the urethane polymer produced has the average formula:—



wherein D is the residue of a dihydroxy compound having a low solubility in the aliphatic hydrocarbon solvent and n is 1-3.

35 10. A process as claimed in claim 9 wherein n is 2.
11. A process as claimed in claim 9 or 10 wherein substituent D is derived
from an aliphatic diol having from 2 to 4 carbon atoms.
12. A process as claimed in claim 10 or 11 wherein the diol has 2 carbon
atoms.
13. A process as claimed in any of the preceding claims wherein the primer
from the condensation reaction of an isocyanate, a mono-hydroxy compound
having from 10 to 22 carbon atoms and an aliphatic diol having from 2 to 6 carbon
atoms.
40 14. A process as claimed in claim 13 wherein the isocyanate for the primer is
hexamethylene diisocyanate, diphenylmethane diisocyanate, tris(4-isocyanato-
phenyl)methane or tolylene-2,4-diisocyanate, optionally containing a proportion
of the 2,6-isomer.
45 15. A process as claimed in claim 13 or 14 wherein the mono-hydroxy
compound for the primer is n-octanol, n-decanol, n-dodecanol, n-octadecanol,
myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol or behenyl alcohol.
50 16. A process as claimed in any of claims 13 to 15 wherein the aliphatic diol
for the primer is ethylene glycol, propane-1,2- or -1,3-diol, an isomer of butane-,
pentane- or hexane- diols, diethylene glycol or thiodiglycol.
55 17. A process as claimed in any of claims 13 to 16 wherein the primer is a
condensation product of tolylene diisocyanate, oleyl alcohol and ethylene glycol.

18. A process as claimed in any of the preceding claims wherein the primer is chemically identical with the urethane polymer produced in the process. 5

19. A process as claimed in any of the preceding claims wherein the process is effected at a temperature within the range of from 80° to 120°C. 5

20. A process as claimed in claim 19 wherein the process temperature is within the range of from 90°C to 105°C. 10

21. A process as claimed in any of the preceding claims wherein the initial solvent level is 20% weight/weight on the total weight of the reaction mixture with subsequent dilution to 40% to 50% weight/weight at the end of the process. 10

22. A process for the production of urethane polymer, as claimed in claim 1, substantially as described with reference to any of the Examples. 15

23. A urethane polymer when produced by a process claimed in any of the preceding claims. 15

24. A pigment dispersion comprising a pigment and, as stabiliser, a solution of a urethane polymer as produced in claim 1. 15

25. A dispersion as claimed in claim 24 wherein the pigment is an azo or azomethine pigment, a metal- or metal-free phthalocyanine, an optionally halogen-substituted polycyclic pigment, a red or yellow iron oxide pigment, a carbon black pigment or a salt of a basic pigment precipitated with heteropoly acid or phosphorous, tungsten or molybdenum. 20

26. A dispersion as claimed in claim 24 to 25 wherein the amount of the urethane polymer is within the range of from 5% to 200% by weight based on the pigments in the dispersion. 20

27. A dispersion as claimed in any of claims 24 to 26 wherein the dispersion contains from 10% to 60% by weight of pigment, based on the total weight of the dispersion. 25

28. A pigment dispersion as claimed in claim 24 substantially as described with reference to any of the Examples. 30

29. A process of producing a pigment dispersion as claimed in claim 24 comprising blending the pigment and the stabilizer components. 30

30. A process as claimed in claim 29 wherein one of the following techniques is employed to effect the blending:— 30

- (a) Ball-milling a mixture of pigment, organic solvent and urethane polymer solution for an extended period. 35
- (b) Flushing the pigment from aqueous press-cake into solvent and then adding the urethane polymer at this stage. 35
- (c) In-situ preparation of the urethane polymer from its starting-materials during the treatment of pigment as in either of steps (a) or (b). 35

31. A process of producing a pigment dispersion as claimed in claim 29 substantially as described in any one of the Examples. 40

32. A pigment dispersion when produced by a process claimed in any of claims 29 to 31. 40

T. SHARMAN,
Agent for Applicants.